^{29}Si AND ^{1}H NMR STUDY OF WATERPROOFING POLYMERIZATION

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1. INTRODUCTION

Lime mortar, is characterized by high porosity, low mechanical strength, good workability, etc. Such properties make it vulnerable to physical, chemical and biological attack.

This vulnerability is directly related to the physical properties of the material, high porosity among them. The water is one of the causes of high lime mortar porosity. Pozzolanic substances may be added to reduce porosity, and lower the possibility of chemical attack[1]. Where mortar porosity cannot be reduced, surface coatings are applied to repel water. Since such products are applied to the outermost surface, they are the components most liable to deteriorate. Due to the small amounts involved, however, it is difficult to determine when they have deteriorated and should be replaced, an issue that is seldom addressed in the literature[2,3]. Spectroscopic techniques can be used to study coatings. The reactivity of siliceous consolidants used to conserve porous cultural heritage materials was studied by Zenndri et al[4], using ^{29}Si NMR, indicating that ethyl silicate exhibited greater reactivity than colloidal silica. Carmona-Quiroga et al[5]. studied by ^{29}Si NMR the interaction between antigraffiti and cement mortar revealing that anti-graffiti products reacted with C–S–H gel, raising the relative proportion of Si in Q^2 positions. Domingo et al[6] stablished the best conditions for Raman and FTIR to study consolidants and water repellent treatments.

[1]Fortes-Revilla and Blanco-Varela, “Influence of water-repellent treatment” 39-52.
[2]Ribas, Silva and Prieto, “Durability of water-repellents” 5-14.
[3]Ferreira-Pinto and Delgado-Rodríguez, “Durability of water repellents”
[4]Zendri, et al. “Characterization and reactivity of consolidants” 1098-1106.
[5]Carmona-Quiroga et al., “Interaction between anti-graffiti and cement mortar” 723–730.
[6]Domingo et al. “Polymerization silicon-based water repellents” 5–12.

In the present study ^{29}Si and ^{1}H NMR were used to characterize different waterproof coatings before and after their application into lime mortars. Polymerization reactions were studied after curing of the waterproof products in open air over an evaporating dish, without interaction with the substrate. Interaction and polymerization of the coating over the lime mortar was also studied by the same spectroscopic technique.

2. METHODS AND METHODOLOGY

The lime mortars were made with a lime:sand 1:1 and a water:lime 0.82. The fresh mortar was poured into 1x1x0.5- moulds and demoulded after 24 hours and stored in a carbonation chamber (21ºC and 50% R.H.) for 1 month.

Two waterproofing materials were used. Thirty ml of product were placed on an evaporating dish and the solvent allowed evaporating (40 ºC, 30% R.H.) to obtain reticulated waterproofing materials[4].

The initial and reticulated waterproofing materials and the lime mortar fully immersed in the waterproofing solution were characterized using ^{29}Si, ^{1}H and NMR. The ^{29}Si and ^{1}H single-pulse MAS spectra were obtained with a BRUKER MSL 400 analyzer. The recording conditions for each of the nuclei are given in Table 01.

TABLE 01

3. RESULTS AND DISCUSSION

The two initial waterproofing substances were characterized by ^{29}Si NMR (Table 02).

TABLE 02

The results confirmed the presence of ethyl silicate in both coatings, being an indication that both products were slightly hydrolyzed. The presence of $RSi(OMe)_3$ in the first product makes it an alkyl-methoxy-silane, whereas the second is a polymethyl siloxane, with $(CH_3)_3Si(O-)$ groups. The alkyl group in product 1 is a terbutyl.

Two clearly differentiated areas can be distinguished on the spectrum of the product 1 reticulated on evaporating dish (Fig.01), at -49 to -70 and -90 to -110 ppm. The former contains signals for terbutyltrimethoxysilane with one (-49.0), two (-57.2 ppm) and three (-66-7 ppm) degrees of polymerization. The four signals in the second zone differ in intensity and correspond to ethyl silicate, non-polymerized and in

different stages of hydrolysis and polymerization. The most intense signals were found for ethyl silicate with three (-101.5 ppm) and four (-110.0 ppm) degrees of polymerization.

FIGURE 01

Deconvolution of the ^{29}Si NMR spectra (Fig.02) shows that 10% of the terbutyltrimethoxysilane formed dimers, 47% linear chains and the remaining 43% reached the highest degree of polymerization. Nineteen per cent of the ethyl silicate, in turn, polymerized to degree two, 48% formed branched chains and 33% form a three-dimensional silicate. Neither of the two active compounds underwent total polymerization.

FIGURE 02

The ^{1}H MAS NMR spectrum for reticulated product 1 (not showed) showed a very wide signal at 1.1 ppm (protons in the methyl and methylene groups) and a shoulder peaking at 3.8 ppm (the ethoxy group proton in the ethyl silicate). Similarly, the spectrum ^{29}Si MASNMR of reticulated product 2 (Fig.01) showed a widening of bands in the -90 to -110 ppm zone, (ethyl silicate polymerization region). The bands ^{1}H MAS NMR in the second product shows an intense band at 0.3 ppm, attributed to the proton in the CH_3 group attached to the Si. The two small bands (1.0 and 1.4 ppm) were generated by the proton in the CH_3 group in $-OCH_2CH_3$. Finally, two other bands at 4.5 ppm (narrow) and 7.1 ppm (wide) were attributed to silanol group hydrogen bonds.

The ^{1}H NMR-MAS spectra for the mortars treated with different waterproofing products shows two new signals at 4.8 and 6.2 ppm in product 1 (Fig.03) from hydrogen bonds between silanol groups. In product 2 (Fig.03), the broadness of the signal in the 3-8 ppm interval, can be due to the hydrogen bonds formed between silanol groups.

FIGURE 3

Deconvolution of the ^{29}Si NMR spectra of the product 1 shows two components, centred over -66 and -78 ppm. The first was assigned to terbutyltrimethoxysilane with three degrees of polymerization ($RSi(O\text{-})_3$), an indication that total polymerization was reached, whereas the second corresponded to ethyl silicate with one degree of polymerization ($Si(OEt)_3(O^-)$ and $Si(OEt)_2(OH)(O^-)$), signifying that total polymerization was not reached. These findings agree with Zendri et al.[7] who observed that ethyl silicate underwent greater polymerization in the presence of $CaCO_3$.

The ^{29}Si CPMAS NMR spectrum findings for product 2 applied to mortar, two signal zones were observed, one in the 0-30 ppm range and a higher intensity envelope in the -46 and -116 ppm interval (Fig.02). The deconvolution of these two zones yielded signals centered over 10 ppm and -86 ppm, corresponding to a polymethylsiloxane in dimer form and ethyl silicate with one degree of polymerization.

4. CONCLUSIONS

1.- Product 1 is a mixture of terbutyltrimethoxysilane (31% polymerized) and ethyl silicate.

2.- The two initial compounds in product 1 polymerized on evaporating dish to different degrees, 43% of the terbutyltrimethoxysilane and 33% of the ethyl silicate.

3.- Product 1 polymerized more on lime mortar than on evaporating dish, (60% terbutyltrimethoxysilane and 40% ethyl silicate).

4.- Product 2 is a mixture of polymethylsiloxane and ethyl silicate. Initially 86% of the ethyl silicate and 100% of the polymethylsiloxane were in monomeric form.

5.- Polymethylsiloxane failed to polymerize on evaporating dish, whereas 86% of the ethyl silicate formed polymers. The product applied to lime mortar, 80% of the ethyl silicate polymerized to the highest possible degree and polymethylsiloxane began to polymerize.

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